

PREDICTION OF LIQUID-VAPOR EQUILIBRIA FROM AN EMPIRICAL
EQUATION OF STATE FOR MIXTURES*

by

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1. INTRODUCTION

This report sets forth a method of calculating the equilibrium phase boundary for which one needs only an equation of state for mixtures and the set of accompanying constants for each of the pure components.

The advent of high speed automatic calculating machines has made feasible the extensive calculations necessary to determine the pressure, volume, temperature and mole fraction properties of a multicomponent system at the liquid-gaseous phase boundary. Connolly, Frankel, and Sage¹ have developed a method of determining the phase boundary utilizing the International Business Machine Electronic Calculating-Punch 604. This method, however, uses experimental data as initial guesses, making a calculation, and then proceeding in an iterative process. The data is available for only a relatively few of the possible systems and therefore the method is of limited applicability.

¹ T. J. Connolly, S. P. Frankel, and B. H. Sage, Report No. 3036, American Documentation Institute, Washington, D. C., (1951).

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II. THEORY

It has been shown by the arguments of thermodynamics² that the necessary and sufficient conditions for equilibrium are:

$$\begin{aligned} P_G &= P_L \\ T_G &= T_L \\ \mu_{iG} &= \mu_{iL} \quad (i = 1, 2, \dots, n) \end{aligned} \quad (1)$$

Where:

P is the pressure of the phase.

T is the temperature of the phase.

μ_i is the chemical potential of the i th component.

The subscripts G and L refer to the gaseous and liquid phases respectively.

From this set of equations the P - V - T and mole fraction properties of the liquid and gaseous phases at the boundary can be uniquely determined if an equation of state for mixtures is assumed, the chemical potential being evaluated from the equation of state³.

The particular equation of state used was that devised by Benedict, Webb, and Rubin⁴. The form of the equation given below refers to one mole

² J. W. Gibbs, "Equilibrium of Heterogeneous Substances", Collected Works, 1, 56, Longman, Green and Co., New York, (1928).

³ J. A. Beattie, Phys. Rev., 36, 132 (1930).

⁴ M. Benedict, G. B. Webb, and L. C. Rubin, J. Chem. Phys., 8, 334, (1940); 10, 747 (1942).

of substance:

$$P = RTd + (B_0 RT - A_0 - C_0/T^2)d^2 + (bRT - a)d^3 + \frac{1}{6}d^6 + (c/T^2)d^3 \left[(1 + \sigma d^2) e^{-\sigma d^2} \right] \quad (2)$$

in which:

P is the pressure in atmospheres.

R is the gas constant,

T is the temperature in degrees Kelvin,

d is the density in mole per liter.

The constants $-B_0$, A_0 , C_0 , b , a , c , α , σ - are determined from the constants for the pure components - B_{oi} , A_{oi} , C_{oi} , b_i , a_i , c_i ,

α_i , σ_i - and their respective mole fractions (x_i) in the following way⁴:

$$\begin{aligned} B_0 &= \frac{1}{6} \sum_{ij} x_i x_j (B_{oi}^{1/3} + B_{oj}^{1/3})^3 \\ A_0 &= \left(\sum_i x_i A_{oi}^{1/2} \right)^2 \\ C_0 &= \left(\sum_i x_i C_{oi}^{1/2} \right)^2 \\ b &= \left(\sum_i x_i b_i^{1/3} \right)^3 \\ a &= \left(\sum_i x_i a_i^{1/3} \right)^3 \\ c &= \left(\sum_i x_i c_i^{1/3} \right)^3 \\ \alpha &= \left(\sum_i x_i \alpha_i^{1/3} \right)^3 \\ \sigma &= \left(\sum_i x_i \sigma_i^{1/2} \right)^2 \end{aligned} \quad (3)$$

The chemical potential determined using equation 2 is:

$$\begin{aligned} \mu_i = & \mu_i^0 + RT \ln(dx_i RT) + d \left\{ \frac{1}{4} RT \sum_j x_j [(B_0)_j]^{1/2} + (B_0)_i^{1/2} \right\}^3 \\ & - 2[A_0(A_0)_i]^{1/2} - (2/T^2)[C_0(C_0)_i]^{1/2} \} \\ & + \frac{2}{3} d^2 [RT(b^2 b_i)^{1/3} - (a^2 a_i)^{1/3}] \\ & + \frac{2}{3} d^3 [a(a^2 a_i)^{1/3} + a(a^2 a_i)^{1/3}] \\ & + \frac{3(C^2 C_i)^{1/2}}{T^2} d^2 \left[\frac{1 - e^{-rd^2}}{rd^2} - \frac{e^{-rd^2}}{2} \right] \\ & - \frac{2C(\gamma_i)^{1/2}}{T^2} d^2 \left[\frac{1 - e^{-rd^2}}{rd^2} - e^{-rd^2} - \frac{re^{-rd^2}}{2d^2} \right] \end{aligned} \quad (4)$$

in which μ_i^0 is the chemical potential of the i th component at P_0 and T_0 of the standard state.

μ_i' , defined below, was used in the calculations and gives the deviations from ideality of the particular system:

$$\mu_i = \mu_i' - \mu_i^0 - RT \ln(RT) \quad (5)$$

III. SYSTEM STUDIED AND METHOD

The binary system of n-heptane (component 1) and nitrogen (component 2) was investigated. The sets of constants used for the pure substances are listed in table 1. The mole fraction of n-heptane is designated as "x" and the mole fraction of nitrogen as "1 - x" since:

$$\sum_i x_i = 1 \quad (i = 1, 2) \quad (6)$$

TABLE I

The constants for nitrogen and n-Heptane used in the Benedict-Webb-Rubin equation of state.

	n-heptane ⁵	nitrogen ⁶
B_{ci}	0.199005	0.0458000
A_{oi}	17.5206	1.19250
$C_{oi} \times 10^{-6}$	4.74574	0.0583907
b_i	0.151954	0.00196154
a_i	10.00475	0.0149000
$c_i \times 10^{-6}$	2.47000	0.000548064
α_i	0.00435611	0.000291545
σ_i	0.0900000	0.00750000

⁵ M. Benedict, G. B. Webb, L. C. Rubin, and L. Friend, Chem. Eng. Prog., 47, 421, table 1 (1951).

⁶ A private communication from Dr. Manson Benedict.

To solve the set of equations:

$$T_G = T_L \quad (7)$$

$$P_G = P_L \quad (8)$$

$$\mu'_{1G} = \mu'_{1L} \quad (9)$$

$$\mu'_{2G} = \mu'_{2L} \quad (10)$$

T and P were chosen equal across the phase boundary. The pair of mole fraction of n-heptane (x_G and x_L) which satisfy equation (9) and (10) at the given T and P were determined by the method of repeated plotting on a larger scale⁷ of μ'_1 and μ'_2 (of both phases) as functions of x_G and x_L . Sets of x's were chosen for both the liquid and vapor phases which bracketed the answers. These x's were then used to compute μ'_1 and μ'_2 for the P and T under consideration. The approximate solution of the simultaneous equations was determined from the graph by inspection. These values of x_G and x_L were then used to choose sets of more closely spaced x's which were in turn used to evaluate the μ'_1 and μ'_2 at the given P and T. Figure 1 shows the last approximation to x_G and x_L at 498.130 and 100 atms.

μ'_1 and μ'_2 were calculated with the aid of the International Business Machine Model I Card-Programmed Electronic Calculator for a given x, P and T from equations (2), (3), and (4). The programming deck of cards used in the calculator first determined the density (d) from equations (2) and (3) by four iterations of the Newton Raphson method⁸. This value of d, along with the given x and T, was then used to determine μ'_1 and μ'_2 from equations (3) and (4).

⁷ J. B. Scarborough, Numerical Mathematical Analysis, p. 190, The Johns Hopkins Press, Baltimore (1950).

⁸ Ibid., p. 203.

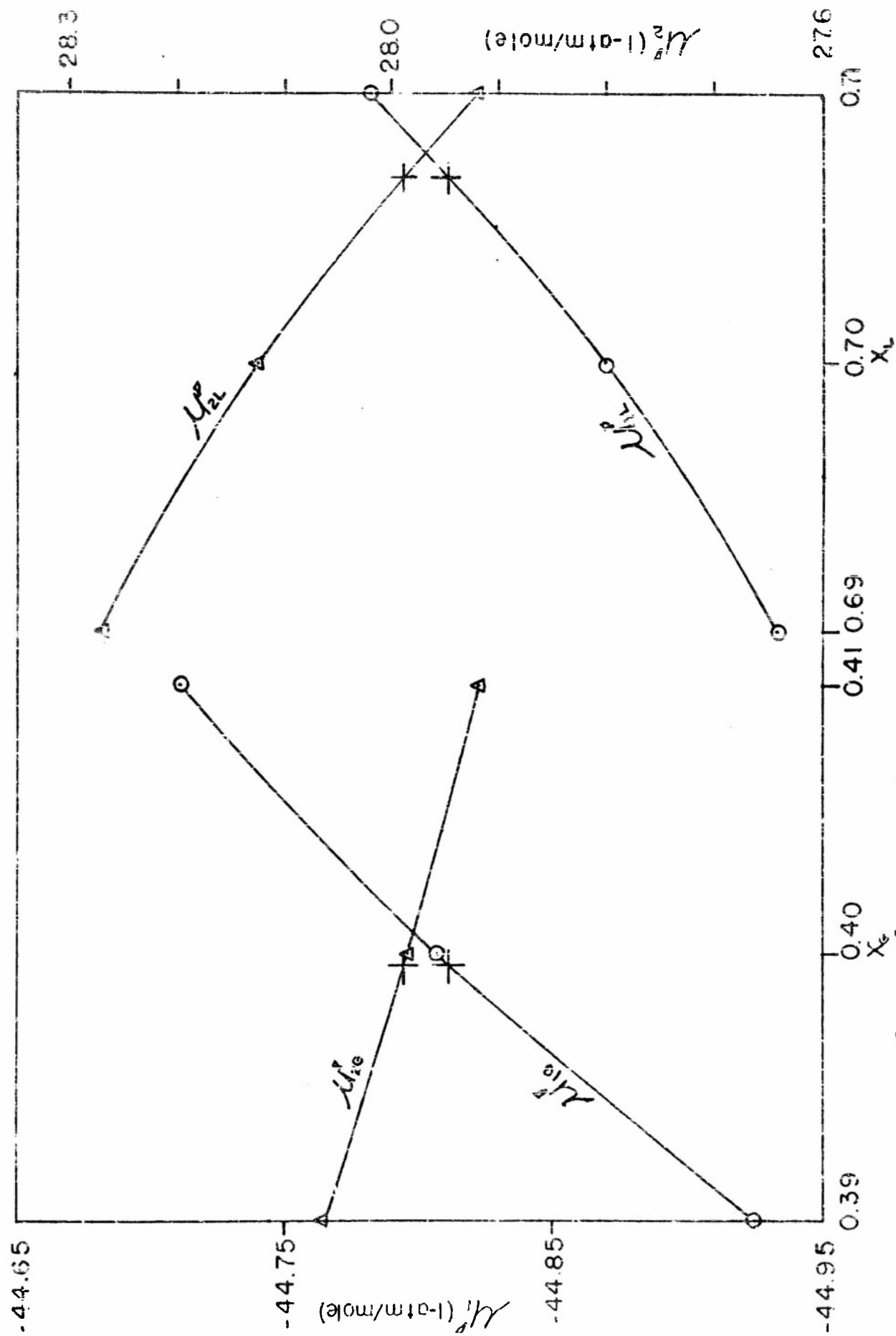


Fig. 1. μ_1^T and μ_2^T at 498.13° and 100 atms. are given as functions of x_0 and x_L . The approximate solutions are indicated by the crosses.

IV. RESULTS AND DISCUSSION

Four temperatures were investigated: 298.13°K, 373.13°K, 448.13°K, and 498.13°K. The results are plotted in figure 2 and listed in table 2. The results at 298.13°K were compared with the experimental results of Palmer, Hirschfelder, and Boyd at 295.6°K⁹. The comparisons, listed in table 4, were made by plotting $\ln(x)$ as a function of $1/T$ for a particular pressure and extrapolating to $1/295.6^\circ\text{K}$. The probable error of the calculated x_G compared to the experimental results is 0.004. The experimental results of Boomer, Johnson and Piercey for the n-heptane-nitrogen system are in disagreement with the results of this work. The mole fraction of n-heptane in the vapor phase at 298.13°K obtained by Boomer, Johnson and Piercey¹⁰ was 0.0104 as compared to 0.002160 for the calculated result.

The range of reliability of the calculated x_G at 298.13°K is from 30 to 250 atm. This limitation is caused by equation (2) failing at densities greater than twice the critical density. This failure is the reason that the upper portion of the $\log P$ versus $\log x$ curve could not be closed and the gas portion of this curve could not be extrapolated to the experimental vapor pressures¹¹ of n-heptane

⁹ H. E. Palmer, J. O. Hirschfelder, and C. A. Boyd, University of Wisconsin Naval Research Laboratory, CM-702 (1952).

¹⁰ E. H. Boomer, C. A. Johnson and A. G. A. Piercey, Can. J. Res., 16B, 396 (1938).

¹¹ S. Young, J. Chem. Soc., 73, 675 (1898).

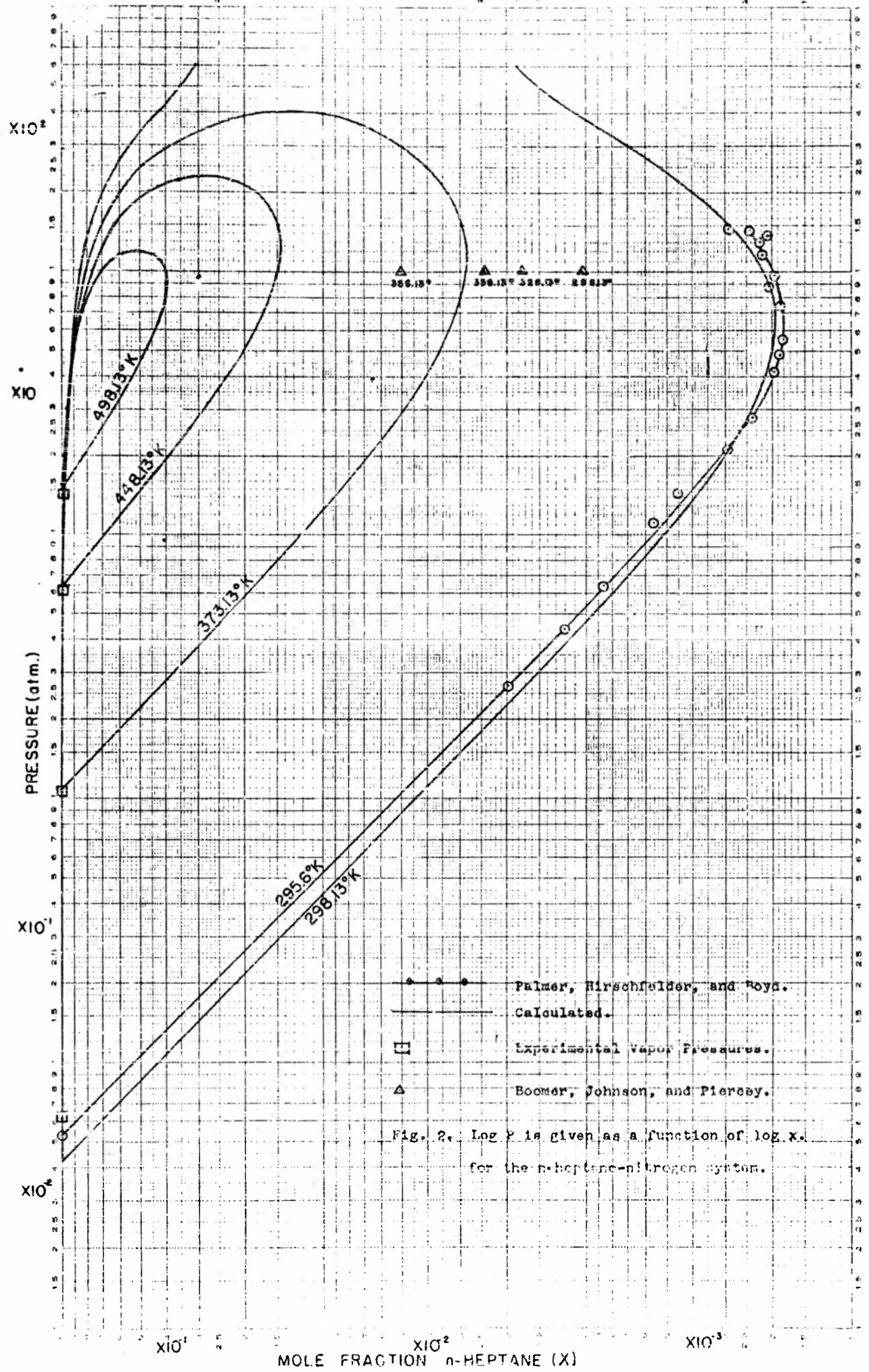


Fig. 2. Log P is given as a function of log x .
for the n-heptane-nitrogen system.

TABLE 2

The results of the calculations for the phase boundary of nitrogen and n-heptane

P (atm)	$X_G \times 100$	$X_L \times 100$	d_G	d_L	μ_1' (1-atm/mole)	μ_2' (1-atm/mole)
298.13°K						
0.2	21.63	99.974	0.008186404	6.68404	-155.313	-123.70
0.5	8.703	99.922	0.020456330	6.686110	-155.294	- 97.38
1	4.392	99.844	0.040910	6.6893	-155.23	- 79.33
5	0.9414	99.19	0.20470	6.716	-154.79	- 39.11
10	0.5131	98.38	0.40981	6.749	-154.24	- 22.07
30	0.2402	95.16	1.23272	6.883	-152.02	4.79
50	0.2002	91.98	2.05560	7.025	-149.79	17.22
70	0.1966	88.85	2.87149	7.145	-147.53	25.44
100	0.2160	84.20	4.07868	7.383	-144.12	34.16
150	0.2862	76.56	5.99793	7.777	-138.31	44.20
170	0.3246	73.52	6.72485	7.945	-136.35	46.97
200	0.3923	69.00	7.76493	8.209	-132.43	51.49
250	0.5306	61.60	9.35527	8.682	-126.45	57.34
300	0.6973	54.45	10.76187	9.197	-120.39	62.31
400	1.090	42.45	13.04954	10.250	-107.96	70.653
500	1.489	34.85	14.7440	11.149	- 95.01	77.760
600	1.810	30.88	16.0136	11.806	- 81.50	84.13

TABLE 2 (continued)

P (atm)	$X_G \times 100$	$X_L \times 100$	d_G	d_L	μ'_1 (1-atm/mole)	μ'_2 (1-atm/mole)
373.13°K						
2	55.10	99.812	0.0675290	5.93204	-104.303	-107.30
3	37.43	99.61	0.100408	5.93887	-104.197	- 79.9
5	23.06	99.21	0.16626	5.9525	-103.98	- 63.1
10	12.20	98.20	0.33029	5.9869	-103.45	- 38.00
25	5.670	95.185	0.8390	6.119	-101.84	- 7.74
50	3.612	90.18	1.63033	6.2740	- 99.142	14.31
70	3.113	86.17	2.2681	6.427	- 96.98	24.94
100	2.864	80.14	3.2043	6.6760	- 93.73	36.24
150	2.957	69.88	4.699	7.117	- 88.33	49.24
200	3.355	59.25	6.1001	7.634	- 82.95	58.67
250	4.021	48.19	7.3980	8.232	- 77.64	66.17
300	5.003	37.11	8.584	8.907	- 72.410	72.478
350	6.568	26.82	9.6445	9.635	- 67.215	78.0073
400	10.5	16.0	10.526	10.451	- 61.96	82.90

TABLE 2 (continued)

P (atm)	$X_G \times 100$	$X_L \times 100$	d_G	d_L	μ'_1 (1-atm/mole)	μ'_2 (1-atm/mole)
448.13°K						
8	82.69	99.59	0.25804	5.16577	- 70.850	-144.9
10	68.90	99.11	0.31428	5.17830	- 70.640	-102.8
12	59.31	98.61	0.37042	5.19094	- 70.435	- 70.05
15	49.39	97.88	0.45459	5.210	- 70.120	- 54.40
25	32.90	95.435	0.7343	5.2740	- 69.08	- 26.15
50	20.28	89.30	1.4272	5.4382	- 66.49	5.35
70	16.95	84.37	1.9745	5.574	- 64.40	19.42
100	14.98	76.78	2.7827	5.486	- 61.31	33.97
150	14.93	63.20	4.099	6.153	- 56.23	49.61
200	18.13	46.19	5.415	6.480	- 51.31	62.00
220	22.21	35.56	6.014	6.506	- 49.404	65.905
498.13°K						
20	82.28	98.420	0.68650	4.4991	- 52.830	- 86.55
50	47.44	89.20	1.509	4.625	- 49.80	- 8.63
100	39.98	70.69	2.999	4.695	- 44.81	27.99
110	42.08	64.91	3.3845	4.606	- 43.8314	32.643
115	44.66	60.28	3.6458	4.4687	- 43.3573	34.7737

TABLE 3
Vapor Pressure of n-heptane

$T^{\circ}\text{K}$	Pressure (atm.)
298.13	0.0612
373.13	1.046
448.13	6.099
498.13	14.38

TABLE 4
Comparison of calculated x_G with the experimental results
of Palmer, Hirschfelder, and Boyd at 295.6°K .

P (atm.)	Cal. $x_G \times 100$	Exp. $x_G \times 100$
150	0.258	0.255
100	0.194	0.198
70	0.175	0.180
50	0.179	0.184
30	0.217	0.227

as the other curves do.

The graphical method of solution developed could be used to obtain any degree of precision desired, but this would not be practical. Rather the results of the graphical method would be used as the initial guesses in an iterative method such as the Newton-Raphson method for simultaneous equations. However, due to the limited accuracy of the Benedict-Webb-Rubin equation of state such extensive calculations are not warranted.

V. CONCLUSIONS

The following conclusions can be drawn from this work:

1. A practical method has been developed by which one can determine the pressure-mole fraction curve of the liquid-gaseous phase boundary for a given temperature from an empirical equation of state.
2. The calculated results from our equation of state, using the constants of the pure components in the equation, are in agreement with the experimental results of Palmer, Hirschfelder, and Boyd, but are in disagreement with the experimental results of Boomer, Johnson and Piercey.